



Department of  
**Environment &  
Conservation**

# Natural Source Zone Depletion

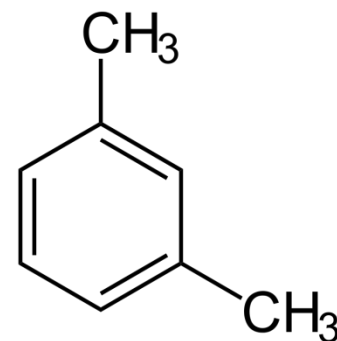
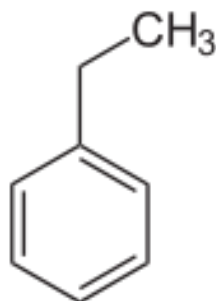
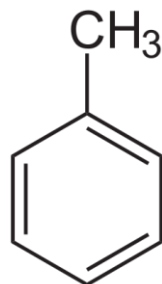
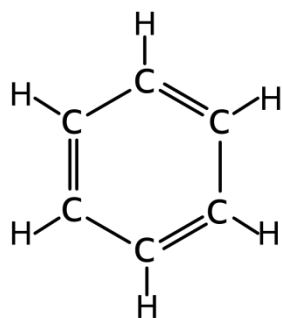
## Environmental Show of the South

Justin Meredith – Division of Remediation

May 17, 2018

# Natural Source Zone Depletion

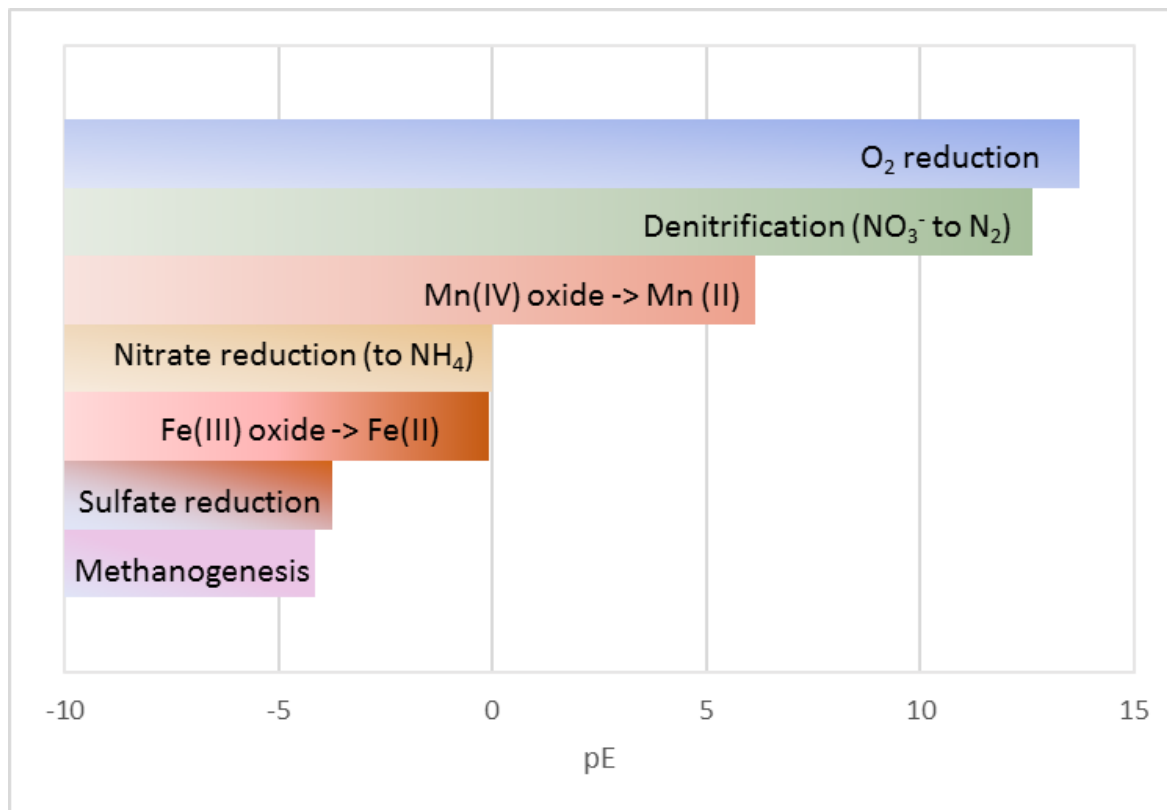
- LNAPL NSZD occurs when a variety of processes act to physically redistribute LNAPL constituents to the aqueous or gaseous phase and subsequently break them down biologically



# Key Aspects of NSZD

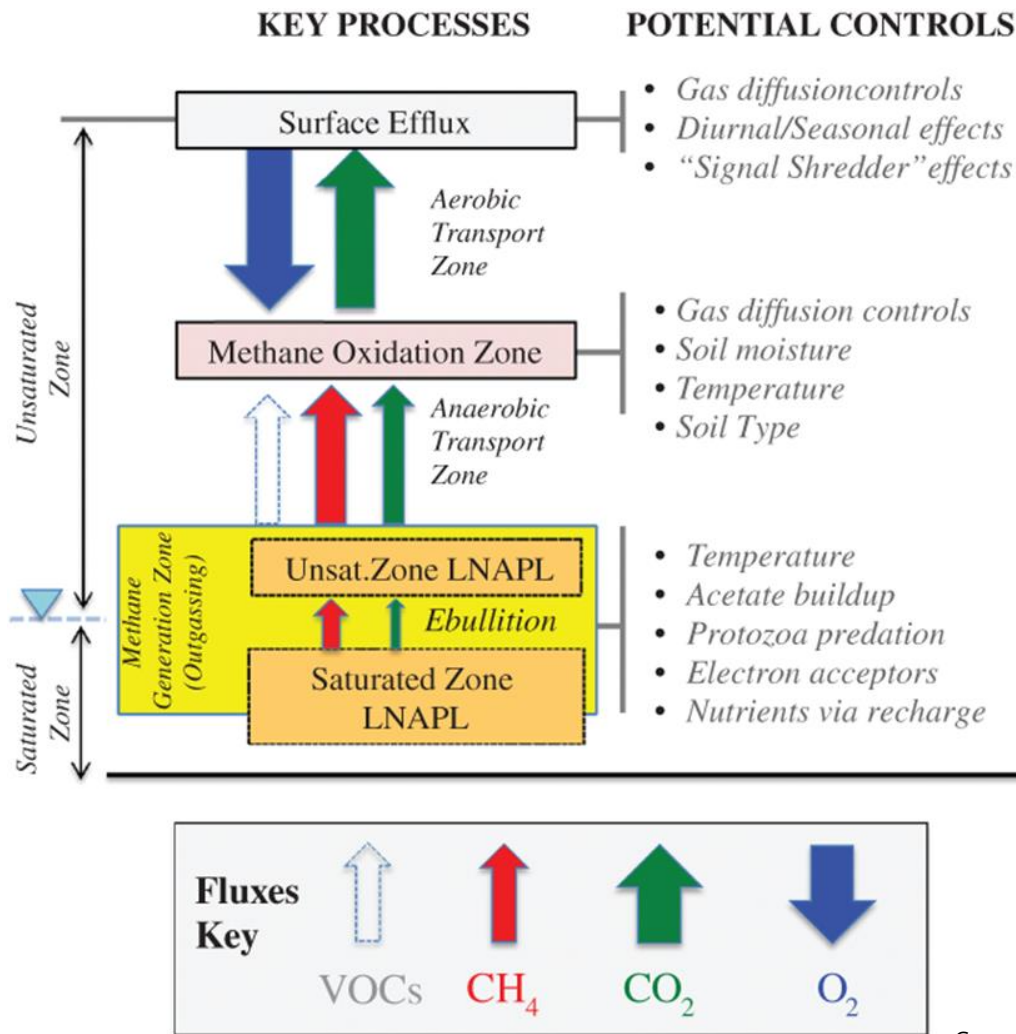
- Rates are a bulk measure
- Direct biodegradation
  - Oil-contact microbiology
  - Observing significant losses of longer chain compounds
- Biogases are directly outgassed
  - >80% of the observed carbon efflux may be attributed to this at Bemidji (Minnesota)
- NSZD rates might be zero-order (constant)

# Terminal Electron Acceptors



ITRC LNAPL-3 NSZD Appendix Figure NSZD-2. Electron acceptor ladder

# EFFLUX



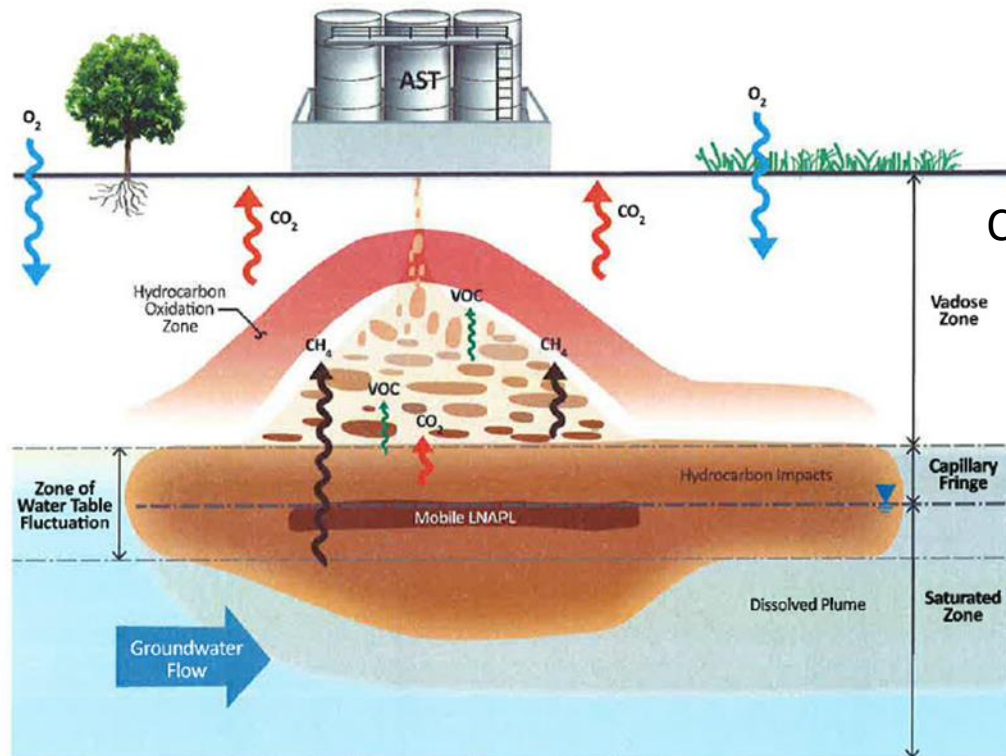
Various processes occurring over space and time

Thermodynamically-driven sequence, first-order biodegradation

Collective effect appears to be a zero order rate

Garg et al., 2017

# Conceptual Model



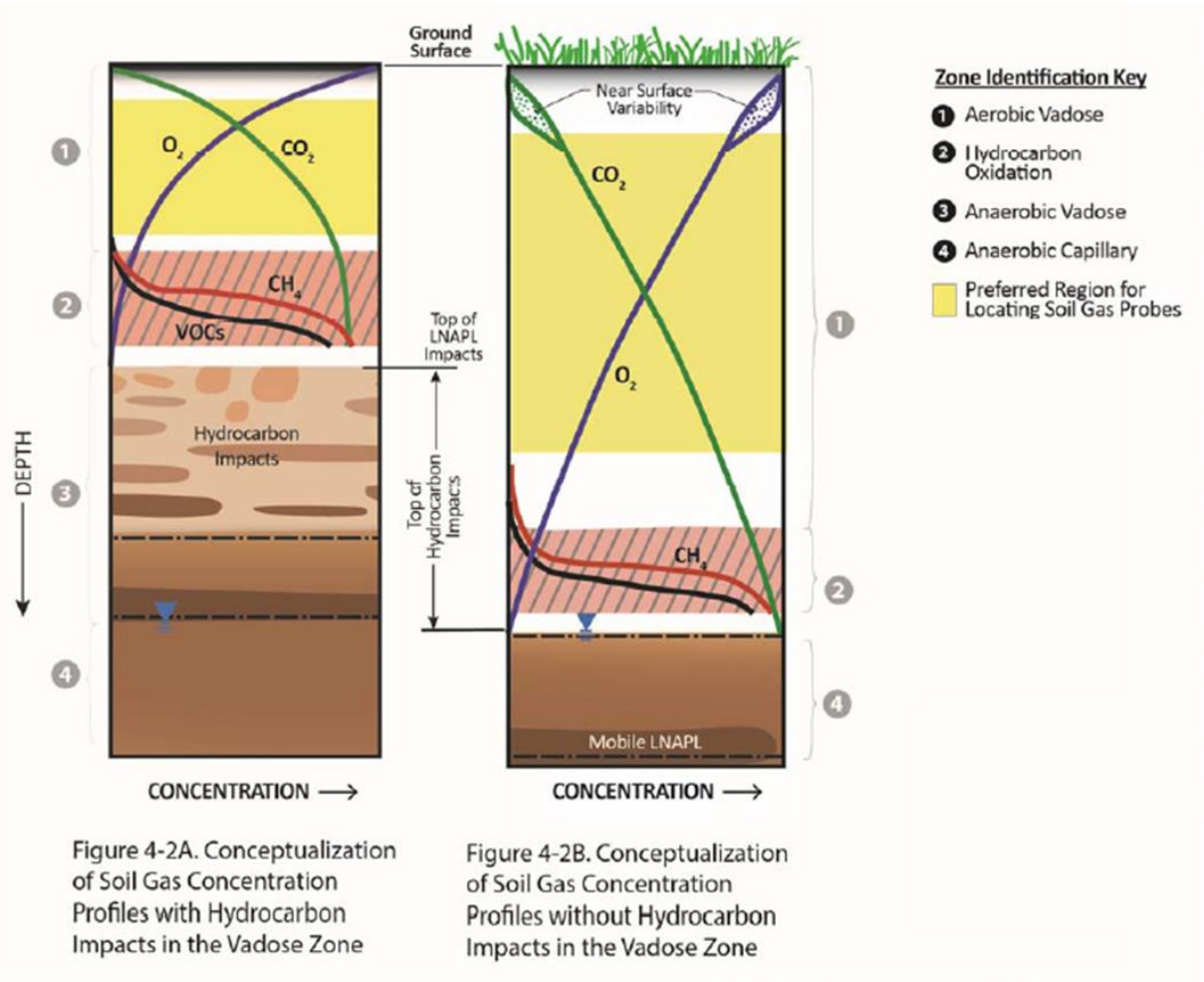
*Note: This is a conceptual depiction of a typical setting and thereby idealizes conditions. No indication of process magnitude is implied by font or arrow size.*

**Figure 1-1. Conceptualization of Vapor Phase-Related NSZD Processes at a Petroleum Release Site**  
NSZD Guidance, American Petroleum Institute

# Method for Measurement

- **Gradient Method** The gas flux is calculated which can then be stoichiometrically converted to equivalent LNAPL mass loss rates.
- **Dynamic Closed Chamber (DCC)** method uses field instrumentation to generate a real-time, short-term direct measurement of soil gas efflux of CO<sub>2</sub>.
- **Passive CO<sub>2</sub> Flux Trap** method uses a chemical “trap” that captures CO<sub>2</sub> emanating from the soil.
- **Biogenic heat** methods are based on the principle that hydrocarbon biodegradation is an exothermic process that produces energy.

# Gradient Method



NSZD Guidance, American Petroleum Institute



# Dynamic Closed Chamber Method

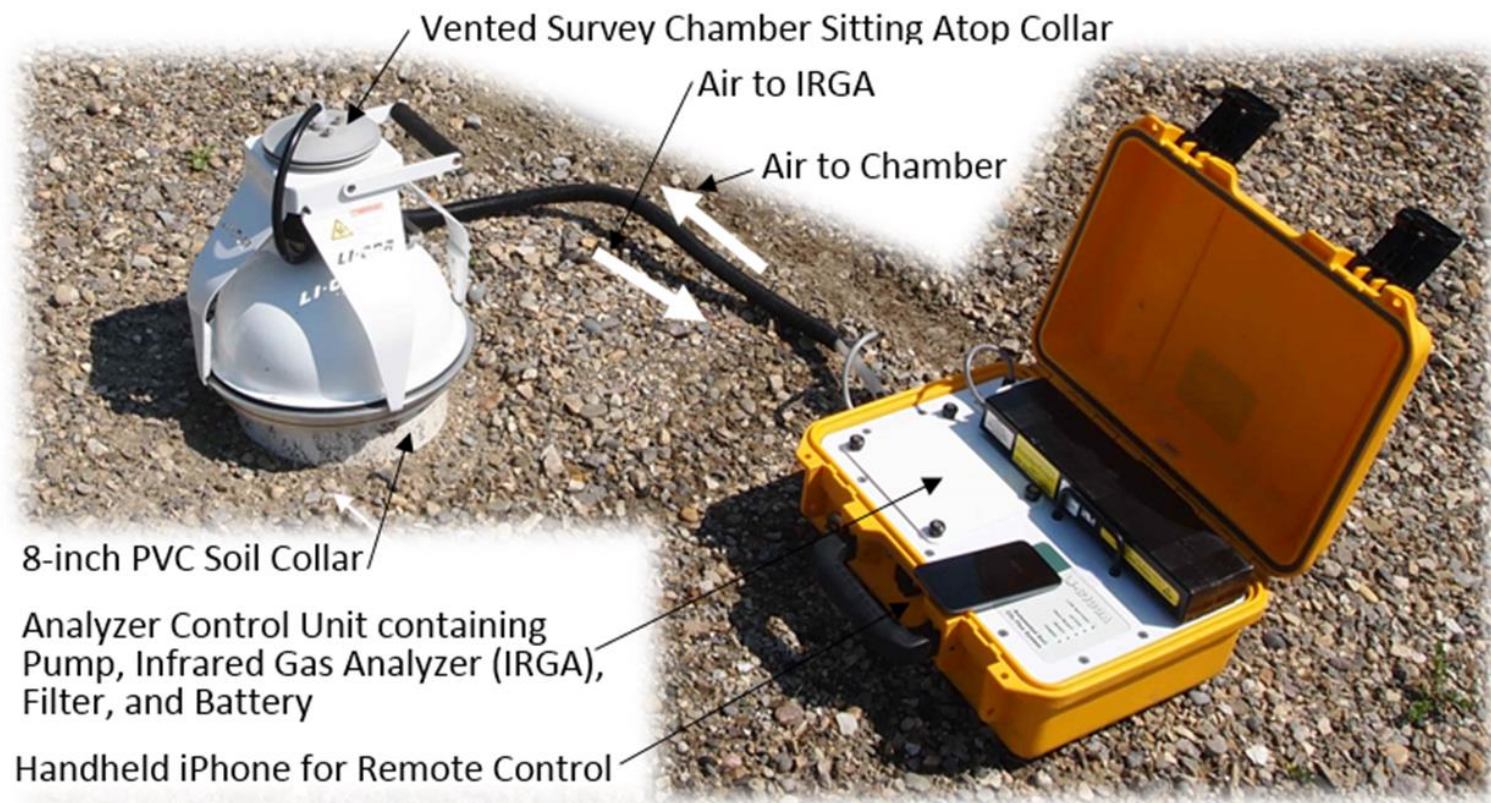


Figure 4. LI-COR 8100A DCC Apparatus and Setup

API, 2017

# Passive Flux Trap Method

The trap has three components: trap body, receiver pipe, and rain cover

Traps are set onto a pre-set 'receiver' pipe (4-inch diameter Sch40 PVC), installed several days in advance; deployment lasts ~ 2 weeks

CO<sub>2</sub> efflux is captured on a sorbent material inside the trap (there is a bottom sorbent layer to collect CO<sub>2</sub> efflux and an upper sorbent material to collect atmospheric CO<sub>2</sub> due to barometric changes)

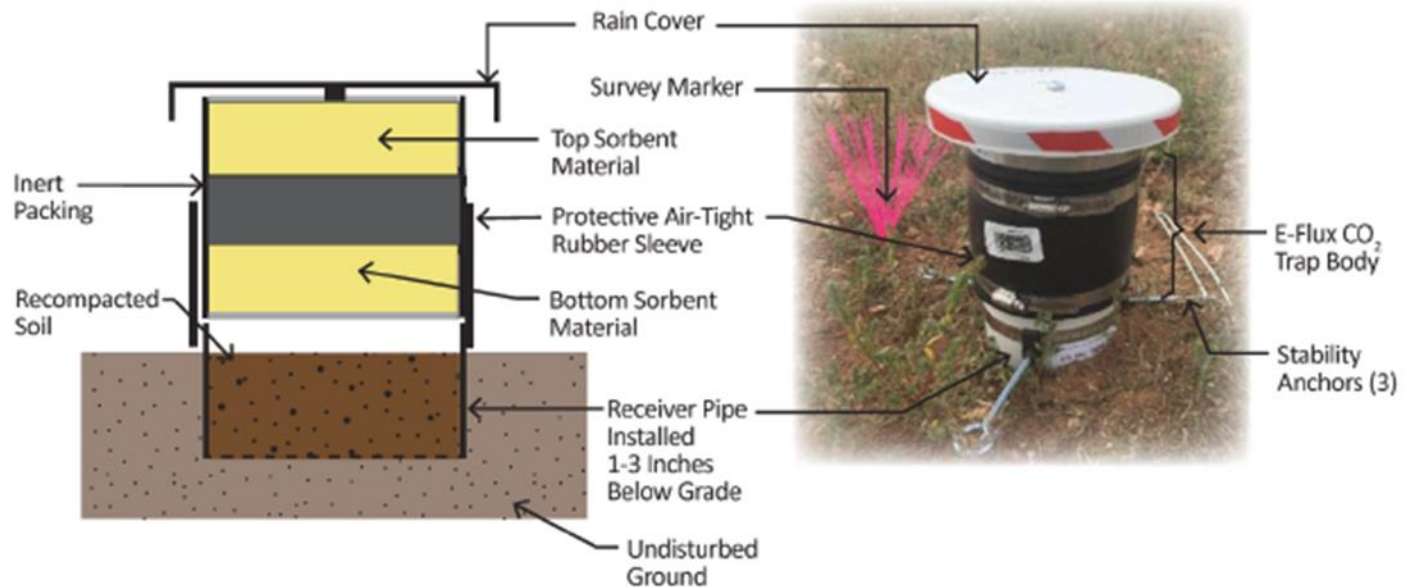
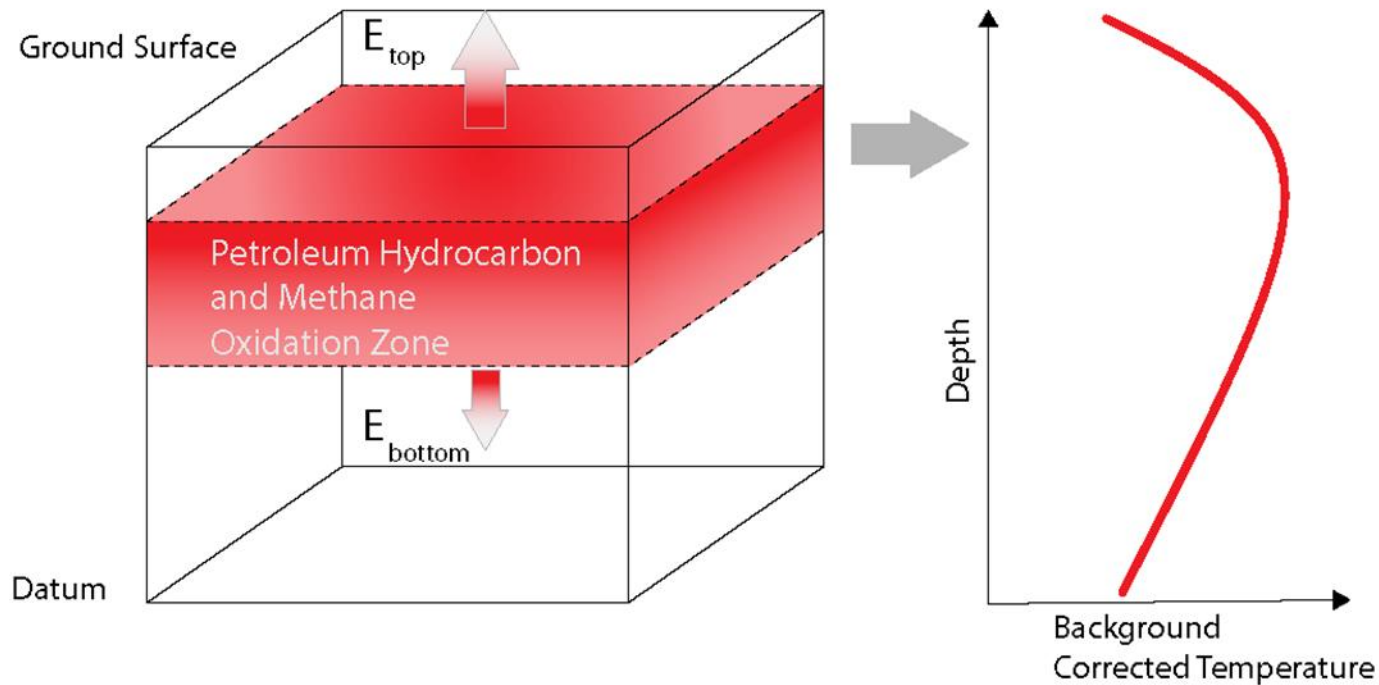


Figure 5-1. Schematic (Left) and Photo (Right) of a Passive CO<sub>2</sub> Flux Trap  
NSZD Guidance, American Petroleum Institute

# Biogenic heat method



*Vertical Profile of Background-Corrected Temperature*

# Background Corrections

- **Flux Trap and DCC** - ( $^{14}\text{C}$ ) correction to differentiate  $\text{CO}_2$  associated with modern (i.e., natural) and fossil (i.e., petroleum NSZD) carbon or a background correction
- **Biogenic heat** - A background correction is required in order to account for natural temperature changes in the subsurface.

# Seasonal Variability

- Continental climate – strong temperature changes
- Corresponds to seasonal variations in contaminant respiration (NSZD)
- CO<sub>2</sub> concentrations begin increasing where oil is present and expand downward from late summer through the fall
- ...indicate an interaction between a seasonally variable process, such as fluctuations in soil temperature, and the presence of oil

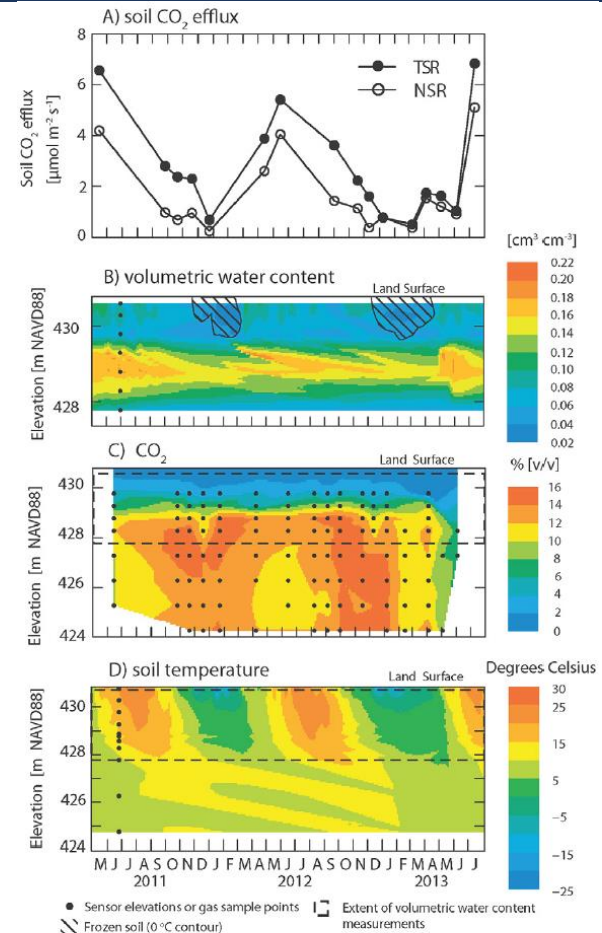


Fig. 11. Field data supporting the conceptual model of vadose zone processes at the Bemidji site: (A) total (TSR) and natural soil respiration (NSR) by the site-average method, (B) daily mean volumetric water content near Well 9015G, (C) vadose zone CO<sub>2</sub> concentrations at Well 9015G, and (D) daily mean vadose zone temperatures near Well 9015G.

Sihota et al., 2016

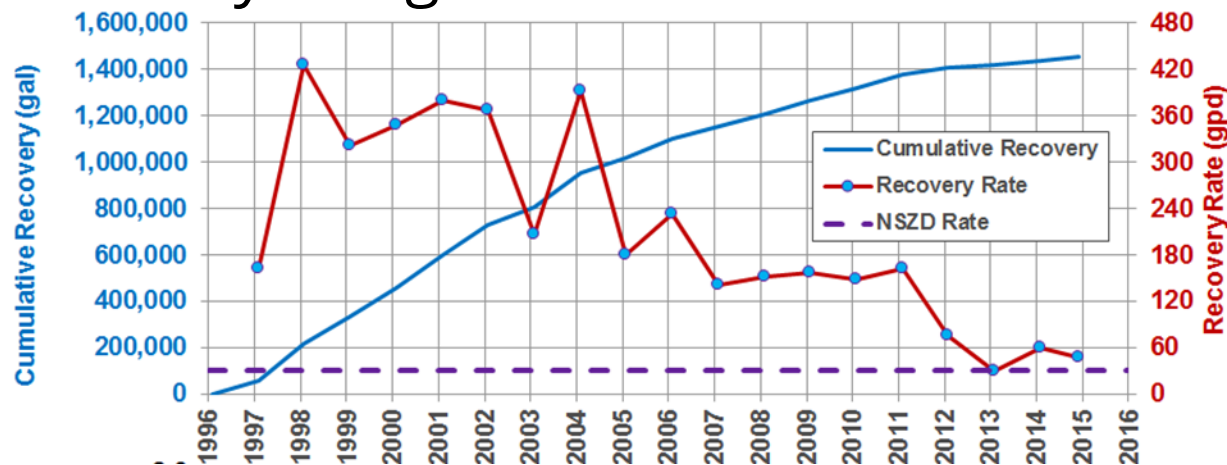
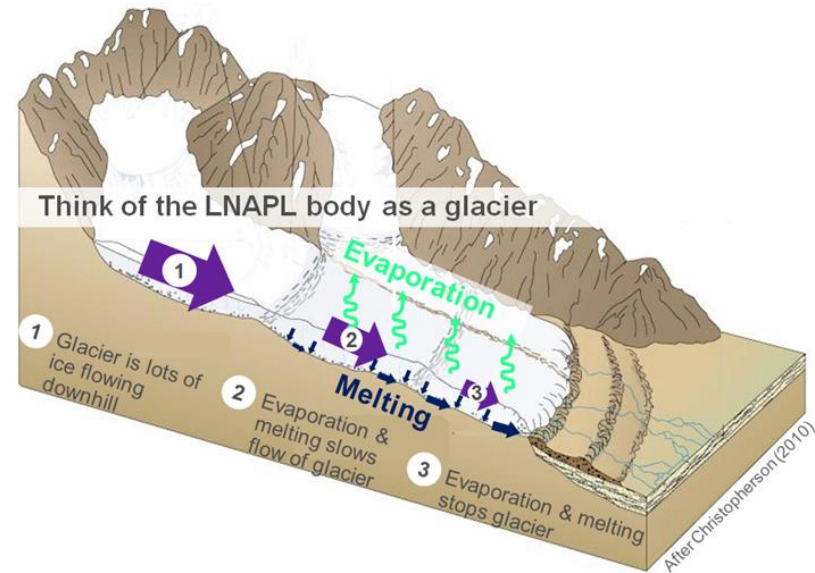


# NSZD at my Site?

- Some Criteria to be Considered
  - Remaining LNAPL and dissolved-phase are not a significant risk to human health or the environment (present or future)
  - NSZD of the LNAPL body and natural attenuation of dissolved-phase plume are documented as occurring and will further mitigate risk from the release
  - Areal extent of plume is shown to be stable or decreasing

# Using NSZD for Decision Making

- LNAPL body stability evaluation
- Practicability determination of LNAPL recovery
- Endpoint metric for active LNAPL remediation
- Benchmark for enhanced-NSZD remedy design



# Where is NSZD Heading

## Research on “non-standard sites”

- Fractured media
  - Shallow
  - Capped
  - Surface water- groundwater interfaces
- AND....
- Risk associated with intermediates?
  - What does the end look like?
  - When will we get there?



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# NSZD - Summary

- NSZD results in mass losses at petroleum hydrocarbon impacted sites
- NSZD mass removal can rival that obtained from engineered remediation, in some cases
- Understanding NSZD rates can help to constrain active remediation endpoints
- Documenting the occurrence and rate of NSZD mass losses is important for understanding it's use as a management alternative